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Impact of the annealing temperature on the optical performances of Er-doped Si-rich Silica systems

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Abstract. Series of Er-doped Si-rich silicon oxide (SRSO:Er) layers were grown by magnetron sputtering at different temperatures from ambient to 500°C and then annealed between 600°C and 1100°C. They were characterized by spectroscopic and time-resolved photoluminescence (PL) measurements. Significant PL was detected at 1533 nm from the as-grown samples at T≥300°C excited by a non-resonant wavelength (476 nm), hence indicating the formation of Si-based sensitizers during the growth process. The PL intensity and the decay lifetime of Er^{3+} ions were both greatly increased with the annealing temperature. An optimum temperature of annealing is obtained at 800°C, which is expected to favor the formation of very dense and small sensitizers. The fraction of Er coupled to sensitizers was found nearly 6-7 times higher than that reported so far in the literature.

1. Introduction

The effective excitation cross section of Er^{3+} ions in SiO_2 is increased by 10^3-10^4 with the insertion of Si-based sensitizers in the matrix. It was shown that an indirect excitation of Er^{3+} ions occurs through Si nanoclusters (Si-nc) [1,2]. Such an energy transfer allows one to benefit from the broadband high absorbance of Si-nc for optical excitation and from the improved transport of carriers injected by electrical excitation. This paves the way to the achievement of Er^{3+} population inversion by either optical or electrical pumping for integrated photonics, such as planar amplifier, laser, etc. Recent studies reported that, in conventional SRSO:Er materials, only a small fraction (<2%) of Er^{3+} ions are effectively benefiting from the Si-nc-mediated excitation [3]. Such a low value is far from ensuring an inversion population of Er^{3+}, but requires, on the contrary, more efforts and studies to enhance significantly the proportion of coupled Er in SRSO:Er samples. These latter are usually submitted to annealing processes to form Si nanoclusters (Si-nc) as sensitizers, to remove non-radiative defects and to activate (optically) the Er^{3+} ions. Such a treatment may change, however, the structure of either the Si-based sensitizers or the Er^{3+} ions. This work aims at investigating the influence of growth and annealing temperature on the optical properties of the SRSO:Er layers and to correlate it to the proportion of Er coupled to sensitizers.

2. Experimental techniques

The samples were grown onto a p type 250 µm-thick silicon wafer with a 5 µm-thick SiO_2 buffer layer. The deposition was made by the magnetron co-sputtering of three confocal cathodes: SiO_2, Si and Er_2O_3, under plasma of pure Argon at a pressure of 2 mTorr. The substrate temperature (T_S) was varied from room temperature (RT) to 600°C. The annealing was achieved under a nitrogen flow, for temperatures (T_a) varying from 600°C to 1100°C during 1 hour. The Si excess was estimated at about

7.5 at% from the analyses of Fourier Transform InfraRed (FTIR) spectra. Er^{3+} concentration was measured by Secondary Ions Mass Spectroscopy (SIMS) and was found to be $2.2x10^{20}$ cm^{-3}. Visible and Infrared (IR) photoluminescence were obtained using the non-resonant 476 nm excitation wavelength from an Ar^{+} laser. Time-resolved measurements were measured thanks to an oscilloscope.

3. Results and discussion

3.1. As-deposited optical properties

Significant Er emission was observed from the as-grown samples with $T_S \geq 300$°C, as illustrated by the typical spectrum displayed in Fig. 1 and recorded with non-resonant excitation wavelength (476 nm). The detection of Er PL at both 1533 nm and 980 nm is indicative of the formation of Si-ncs acting as sensitizers during the grown process when performed with $T_S \geq 300$°C. This is supported by the visible PL band centered at ~750 nm which can be attributed to Si-ncs. Similar Er PL features have been obtained earlier by our group on Er-doped SRSO samples grown with T_S =500°C [4].

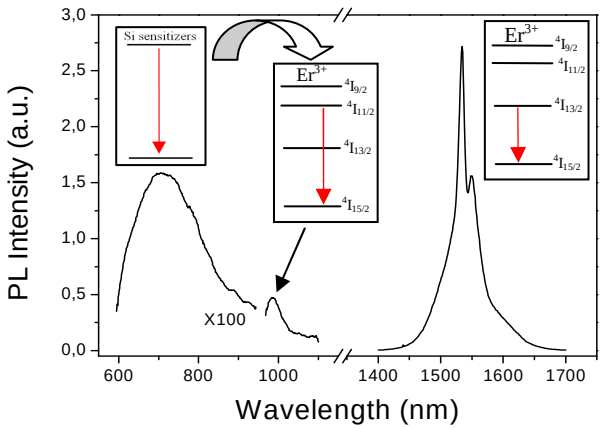

Figure 1.
PL spectrum of the 'as-deposited' SRSO:Er sample. Each electronic transition scheme is enclosed to its corresponding peak. In the range 600-1100 nm, the PL was detected by a Photomultiplier tube while in the range 1400-1700 nm the PL was measured by a nitrogen-cooled Ge detector. The two detectors were calibrated to compare one with the other.

These observations reveal that the Si-based sensitizers are formed during the deposition process. Chosen T_S are high enough to ensure the surface mobility of the adatoms and then the growth of sensitizers on the seeds available at the surface or near-surface region of the growing layer. These Si-based entities play the role of efficient sensitizers *before any annealing treatment*, hence reflecting a favorable environment and good quality matrix. Indeed, the Er^{3+} lifetime was found to be ~4 ms at 1533 nm which is a notably high value for a non-annealed sample, compared to that reported by other groups for annealed samples [5,6]. The lifetime is well fitted by a single exponential decay, suggesting a single kind of site for emitting erbium ions.

3.2. Enhancement of the optical properties by annealing treatment

Figure 2 describes the evolution of the integrated intensity in function of T_a for the two main PL features: the Er^{3+}-PL around 1533 nm and the Si-nc-PL around 700 nm. The annealing treatment improves gradually the Er^{3+} emission until 3 times that recorded from the as-deposited sample when T_a reaches 800-900°C. At higher T_a values, the Er^{3+} emission shows a sharp decrease down to the tenth of the maximum. For the other feature, the Si-related emission appears almost constant for $T_a \leq 1000$°C, before increasing drastically when T_a is further increased to 1100°C. Such an increase of T_a has apparently some counterbalancing effects on the PL of Si-ncs and Er^{3+} ions, suggesting some changes in the transfer mechanism and material structure in this range of annealing. The behavior of the Er^{3+} emission lifetime upon annealing temperature is shown in figure 3. The lifetime is increased with T_a from about 4 ms to a plateau at ~6 ms for annealing between 700 and 900°C.

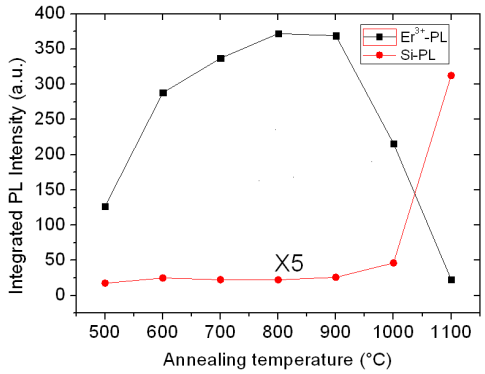

Figure 2. Integrated PL intensity versus annealing temperatures

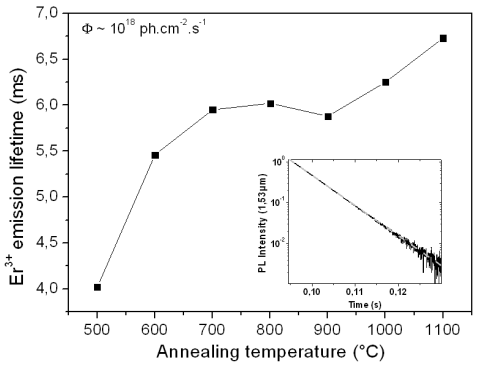

Figure 3. Evolution of the Er^{3+} emission lifetime as a function of the annealing temperatures. The inset shows the characteristic single-exponential behaviour of time-resolved PL spectroscopy.

It shows an additional increase to ~7 ms when T_a is further raised to 1100°C. The behaviour of the lifetime is consistent with the evolutions of the two emissions shown in Fig. 2. The annealing from 600 to 900°C is expected to lead to the following: (i) the growth of additional sensitizers for more coupling with Er ions, especially as the separating distance should be as low as ~0.5 nm for an optimum energy transfer [7,3], (ii) the reduction of the non-radiative channels and then the increase of the lifetime, as observed. On the other hand, the annealing at T_a higher than 900°C may induce some structural changes such as: (i) the coalescence phenomenon that takes place in this range of temperature [8] and which results in larger Si-nc at the expense of their density and then of their coupling with the Er ions, (ii) the diffusion and segregation of Er which might occur in this range of T_a for our Er content, as demonstrated elsewhere [6], (iii) the enhanced diffusion mechanism of other elements such as oxygen could contribute to feed the Er surrounding with more oxygen [9] for further raise of the lifetime. These two suggestions of nanoclusters coalescence and Er segregation can consistently explain the drastic decrease of the Er PL and the counterpart sharp increase of Si-nc PL. The segregation of Er at high values of T_a is supported by the comparison of the evolution of Er PL for T_a =1100°C to that of the as-deposited sample according to the excitation photon-flux ϕ (Fig. 4).

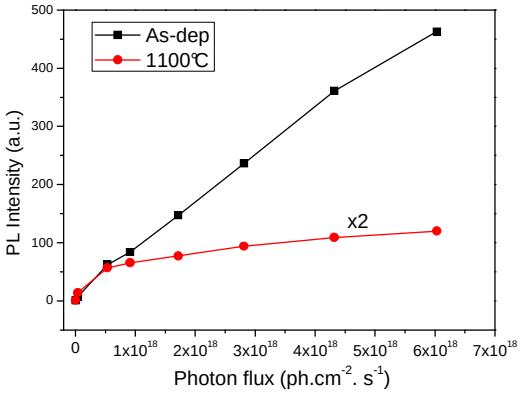

Figure 4. PL intensity of Er^{3+} emission (at 1.53 µm) as a function of the photon flux for as-deposited sample and 1100°C annealing sample.

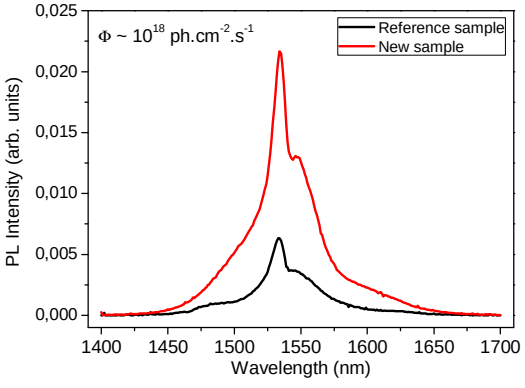

Figure 5. Comparison of the PL Intensity from a reference sample and from our best sample. The reference sample as a known coupling fraction (1.76%)

Indeed, the rapid saturation of the former when ϕ is increased is indicative of an agglomeration of Erbium, as already observed for Er-doped SiO_2 [10] and Er-doped SRSO [11], whereas the latter evolves almost linearly with ϕ. The other impact of T_a = 1100°C lies in the formation of large Si-ncs

that can more easily crystallize and would be limited by a sharp Si/SiO_2 interface containing relatively small amount of defects. They are, therefore, emitting more efficiently in the visible range with a peak shifting towards lower energy (750 nm vs 700 nm for as-deposited, not shown). This explain the abrupt increase of its emission for T_a =1100°C. These structural changes have also an impact on the evolution of the lifetime. It was reported recently that the Er radiative lifetime is affected by the proximity and the size of Si-nc [12]. Ref 12 demonstrates that the shortening of the Er-nanocluster spacing and the size increase of the nanocluster, lead to the lowering of the radiative decay time. In this connection, one can, therefore, consider that the increase of the Er lifetime, particularly for T_a > 900°C (Fig. 3) can also be due to the increasingly reduced impact of Si-nc which grows further away from Er ions.

Finally, to estimate roughly the fraction of coupled Er in our best sample (T_S =500°C, T_a =900°C), we have compared its Er PL to that of a reference sample described in Ref.3 (figure 5) and whose fraction of coupled Er is only 1.7%. This latter contains 4 x 10^{20} Er/cm^3, the same amount of Si excess (7.5 at. %) and was annealed at the same T_a. At a same excitation flux (ϕ ~10^{18} $ph/cm^2.s$), their PL intensity can be compared following $I_{PL} \propto \sigma_{eff}.\phi N_{Er,c}.\tau_{dec}/\tau_{rad}$ where σ_{eff} is the effective excitation cross section, τ_{dec} is the time decay and τ_{rad} is the radiative lifetime. $N_{Er,c}$ is the concentration of Er^{3+} ions coupled to Si-nc, which is equal to about 6.8×10^{18} cm^{-3} for the reference sample. By comparing the ratio of their intensities (~3.6), their σ_{eff} (3.1×10^{-17} cm^{-2} vs ~ 2.3×10^{-17} cm^2), their τ_{dec} (6 ms vs 3.6 ms) and their τ_{rad} (12 ms vs 9 ms) as can be deduced from [13] on the basis of their refractive index (1.56 vs 1.52), one could estimate $N_{Er,c}$ for our best sample to about 2.6×10^{19} cm^{-3}. This value represents nearly 12% of the total Er content (2.2×10^{20} cm^{-3}), i.e. 6-7 higher than that of the reference sample at this photon flux.

4. Conclusions

An efficient indirect excitation of Erbium ions via Si sensitizers was obtained before any annealing treatment, while the optimum Er emission is obtained after annealing in the 700-900°C range. The corresponding lifetime is found as high as 4 ms for the as-grown, and increases significantly with annealing. Structural changes are noticed after annealing at more 1000°C. A rough estimate of the fraction of coupled Er has allowed to notice that their proportion was improved from about 1.7% for earlier samples to nearly 12%.

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